

# Net Average Molecular Orientation during a Full Rotational Period with Single-cycle Pulses

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Although no experimental demonstration exists so far, sub-cycle electromagnetic pulses in the THz region, due to their time asymmetry, are considered to be one of the best options to orient molecules. However, we argue that orientation with half-cycle pulses, in the sudden regime, is an unphysical artifact that arises from a constant component of the field that is not a solution of Maxwell's equations. On the other hand, large instantaneous orientations can be achieved by time-symmetric single-cycle pulses of zero area. We show that, in this case, interferences among eigenstates of the time propagator give rise to a nonzero time average orientation, over the pulse duration, in spite of the existence of time-inversion parity. We also show that, due to the avoidance of the long-tail requirement, multi-single-cycle-pulse schemes can be designed to obtain a net average orientation over a rotational period.

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Rapid experimental developments of cooling methods and intense coherent sources has boosted an extraordinary interest in the understanding of phenomena related to the quantum control of molecular degrees of freedom [1]. In the last decade molecular alignment was one of the areas where impressive success was achieved, with the development of theoretical strategies and the experimental demonstration of several techniques [2]. However, molecular orientation has not progressed at the same speed. Control of molecular orientation with half-cycle pulses (HCPs) has been one of the most intensively studied approaches in the last few years promising that high orientation can be obtained in a very efficient way [3]. Nonetheless, an experimental demonstration of the phenomenon has not been achieved yet.

HCPs interact with the permanent dipole of molecules imparting them a sudden kick that transfers angular momentum, and breaks rotational parity. A molecule in a rotational eigenstate, is guided to a wave packet that contains rotational eigenstates of different parity, and for which the angle formed by the molecular axis and the field polarization vector is well defined. This view is based on a picture in which the HCP consists of a short and strong unipolar part during which a force is exerted on the molecule, and a weak long tail [4] which does not significantly alter the relative populations of the wave packet components. The long tail is required for the pulse to be propagable without considerable distortion because if the field area is not zero the pulse is not a solution of Maxwell's equations [5]. For a sudden interaction the orientation achieved at the end of the unipolar part of the HCP is usually very modest, but during the long tail the phases of the components of the wave packet synchronize producing at some later time a larger orientation. Schemes to maintain high molecular orientation have been devised based on sequences of pulses that impart further kicks at each time the molecules start to lose their maximum orientation [6]. However, they only can work for heavy molecules for which the time to achieve

the maximum orientation is comparable to the duration of the long HCP tail. Therefore, a new pulse can be sent at the correct time without interfering with the previous one. On the other hand, light molecules go through several orientation/missorientation cycles during the tail, and before a new pulse kicks them the orientation is destroyed as shown in the upper panel of Fig. 1. A molecule with rotational constant  $B = 10 \text{ cm}^{-1}$  loses its maximum orientation in less than 100 fs, while a molecule with  $B = 0.1 \text{ cm}^{-1}$  remains oriented around 50 ps, which may be comparable to the tail duration. Thus, the long-tail requirement is an obstacle to obtain persistent orientation except for heavy enough molecules.

Apart from an apparently unnoticed paper by Sugny *et al.* [7], and a recent work by Fleischer *et al.* [8] single-cycle pulses, that do not contain a long tail, have not been studied. Numerical evidence was presented in [7] showing that symmetric pulses of zero area can produce significant instantaneous orientation during and after the pulse is over. In [8] it was experimentally demonstrated that intense single-cycle THz pulses induce field-free orientation that survives thermal averaging. In the present Communication I show that not only large peak orientations but also a nonzero time average orientation during a single pulse of duration comparable to the rotational period can be obtained. This phenomenon is caused by the interference between pairs of eigenstates of the time propagator, as previously described for transport phenomena in quantum Hamiltonian ratchets [9, 10]. Ratchets exhibit directed motion in the absence of an external bias. Recently, it has been shown that ratchet effects can occur in coherent systems such as a Bose Einstein condensate realized with an optical lattice periodically modulated in time [11]. Although this effect requires breaking all spatio-temporal symmetries simultaneously, transient currents can be generated in the presence of some symmetry [9, 12]. A similar mechanism is responsible for transient molecular orientation.

Achievement of molecular orientation has been consid-

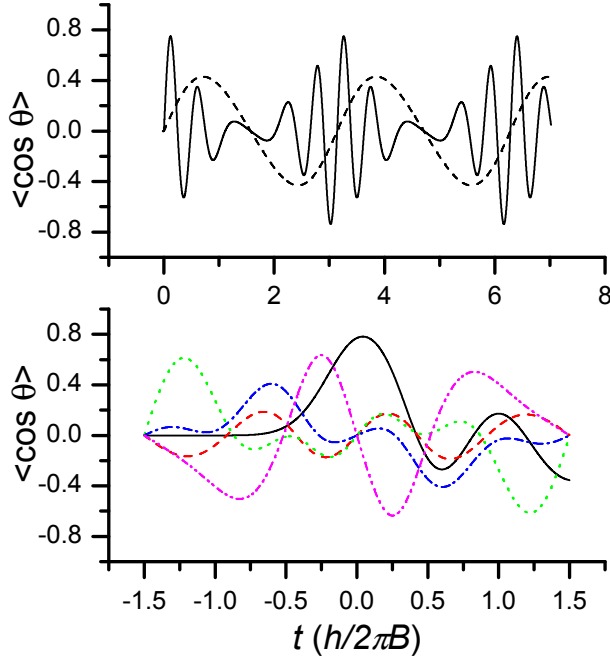


FIG. 1. (Color online). Instantaneous molecular orientation  $\langle \cos \theta \rangle$  produced by THz pulses as a function of time, in reduced units, for a molecule initially in the rotational eigenstate  $|J=0, M=0\rangle$ . Upper panel corresponds to half-cycle pulses with parameters  $\sigma = 0.006(\hbar/B)$ ,  $T = 0.04(\hbar/B)$ ,  $\omega = 200(B/\hbar)$ . In these units a rotational period is  $\pi$ . Solid line is for  $\mu E_0/B = 1000$ , and dashed line corresponds to  $\mu E_0/B = 100$ . When the unipolar part of the HCP ends no orientation is achieved. It is during the long tail that the molecules orient but taking into account that the average orientation, under field-free conditions, over a rotational period is zero, the orientation is lost if the tail lasts longer than the rotational period. In the lower panel the solid line shows orientation for the same initial state, for a zero-area pulse with  $\mu E_0/B = 12$ ,  $\sigma = 0.45(\hbar/B)$ ,  $T = 3(\hbar/B)$ ,  $\omega = 3(B/\hbar)$ . Dash-dotted lines give the orientation of the Floquet states that give a greater contribution to the initial state.

ered traditionally more difficult [13] than the well understood molecular alignment because it requires breakdown of inversion symmetry. Three different schemes have been proposed, (i) combination of a strong nonresonant field and a weak static field [14], (ii) two-color laser schemes with resonant [15] or nonresonant [16] pulses, and (iii) sub-cycle and few cycle THz pulses [17, 18]. It is frequently argued that any orientational effect in molecules requires an external field asymmetric in time. Thus, the highly asymmetric temporal structure of HCPs is considered especially appropriate to achieve orientation. Previous theoretical studies have been based on HCPs consisting of an unipolar part followed by an infinite tail of infinitesimally small negative intensity such that  $\int_{-\infty}^{\infty} E(t)dt = 0$ . Since this tail does not interact with the molecule any possible orientation effect comes from the symmetric unipolar part, that can be written as

$E(t) = E_0 \exp(-(t-t_0)^2/\sigma^2) \cos(\omega t)$ , where  $\sigma$  is related to the Gaussian time width, and  $\omega$  is in the THz region.

Experimentally available HCP pulses of enough strength are short compared to typical rotational periods. Thus, previous works were centered on the sudden regime in which orientation is achieved only after the pulse is over. On the other hand, in the sudden regime, single-cycle pulses do not produce any noticeable orientation, but Sugny *et al.* [7] showed that zero area pulses can produce large instantaneous orientations when its duration is not too short compared to the rotational period. Note, in passing, that longer pulses, in the adiabatic regime, can produce instantaneous orientation too. We show here that in the intermediate regime, but not in the adiabatic regime, the average time orientation during the pulse can be nonzero in spite of the presence of space-time symmetries.

Constraints on the average orientation during a pulse or during several pulses that span a rotational period can be rigorously understood by the existence of dynamical symmetries of the unitary time propagator. These symmetries can be analyzed more conveniently by considering that the pulse is the first member of a periodic sequence of pulses, which allows us to study instead the symmetries of the Floquet Hamiltonian, as both operators have the same eigenvectors [19]. Thus, we will analyze the symmetries of  $U(T/2, -T/2)$  where  $T$  is the repetition period. The Floquet Hamiltonian (in reduced units [20]) for a rotating linear molecule in the presence of a periodic train of linearly polarized pulses, and period  $T$  is

$$\mathcal{F}(t') = J^2 - \frac{\mu E_0}{B} \exp(-t'^2/\sigma^2) \sin(\omega t' + \phi) \cos \theta - i \frac{\hbar}{B} \frac{\partial}{\partial t'}, \quad (1)$$

where  $\phi$ , the carrier envelope phase (CEP), is zero for single-cycle pulses of zero area,  $J$  is the angular momentum vector,  $B$  the rotational constant,  $\mu$  the permanent dipole moment, and  $\theta$  is the angle between the polarization vector of the field and the internuclear axis. Operator  $\mathcal{F}$  acts in the extended Hilbert space where time,  $t'$ , is treated like another spatial variable [21]. Its eigenfunctions can be expanded in the basis of rotational functions  $\langle \theta, \Phi | J, M \rangle$  where  $M$  gives the projection of  $J$  along the polarization direction of the electric field, and  $\Phi$  is another Eulerian angle that defines the direction of  $J$

$$\hat{\chi}(\theta, \Phi, t') = \sum_{J \geq M} \left( \sum_n d_{Jn} \exp(2\pi i n t'/T) \right) \langle \theta, \Phi | J, M \rangle. \quad (2)$$

Formally, eigenfunctions,  $\chi$ , of the Floquet operator  $U$  can be obtained from Eq. (2) by taking the projection  $t' = t = T/2$ . In practice, they can be easily calculated using the generalized Floquet or  $(t, t')$  theory [22], that gives the time evolution operator as the product  $\prod_{m=0}^M U[m\tau + T/2, (m-1)T/2]$  with

$$U(m\tau, (m-1)\tau) = \sum_{n=-\infty}^{\infty} \exp(2\pi i n m \tau / T) \\ \times \left\{ I \delta_{n,0} - i \frac{\tau}{\hbar} [F(\theta)]_{n,0} - \frac{1}{2} \frac{\tau^2}{\hbar^2} [F^2(\theta)]_{n,0} + \dots \right\} \quad (3)$$

where  $\tau$  is a small time interval, and  $F(\theta)$  is the matrix representing the Floquet Hamiltonian. For small enough  $\tau$  the matrix  $U$  can be truncated into a small matrix.

Floquet theory gives us additional advantages over simpler propagation methods in terms of understanding. The method gives direct access to the matrix elements of the different field components, and the influence of a particular component of the electric field can be immediately understood. The Fourier expansion of a HCP pulse ( $\phi = \pi/2$ ) contains a static component, which is the cause of molecular orientation for pulses in the sudden regime as shown in Fig. 2. Dashed lines correspond to calculations in which the static component has been retained showing that large orientation can be obtained regardless of the pulse duration. However, real HCPs cannot have such a nonpropagable dc component. Far from the source, the dc and low frequency components are filtered out distorting the field [23]. The solid lines in Fig. 2 are obtained after eliminating the effect of the static component, which is done by zeroing the terms with  $n = 0$  in Eq. (3). Panels a, and b in the figure show that for short pulses the orientation is almost suppressed. Thus, although previous theoretical studies had attributed molecular orientation by HCPs, in the sudden regime, to their asymmetric structure, the actual mechanism is the existence of an unphysical Stark effect. Longer HCP pulses have a dc component too, but it is relatively weaker than in the sudden regime. In this regime orientation is still possible even if the dc component is filtered out, as shown in panel c of Fig. 2. This component desymmetrizes the Floquet eigenstates, i.e., each one of the Floquet eigenstates that form the initial state may show a net average orientation during the pulse unlike the Floquet eigenstates for a zero-area pulse shown in the lower panel of Fig. 1.

The electromagnetic field for a single-cycle pulse is an odd function of time,  $E(t) = -E(-t)$ . Thus, the eigenvalue equation  $\mathcal{F}(t')\hat{\chi}(t') = \epsilon\hat{\chi}(t')$  is invariant under  $S_{TP} : (\hat{\chi}, \theta, t') \rightarrow (\hat{\chi}^*, \pi - \theta, -t')$ , which is the rotational version of the anti-linear transformation defined in [10]. The transformation  $\theta \rightarrow \pi - \theta$ , is a rotational-restricted version of the operation  $E^*$ , that in molecules inverts the spatial coordinates of all the nuclei and electrons through the molecular center of mass [24]. Symmetry  $S_{TP}$  is called time-inversion parity [10] because it generalizes the notion of parity to the extended Hilbert space. For our system, it implies that if a given Floquet eigenstate is oriented (localized at  $\theta_0$ ) at time  $-t$  it becomes antioriented (localized at  $\pi - \theta_0$ ) at time  $t$ , resulting in a zero time average orientation during the

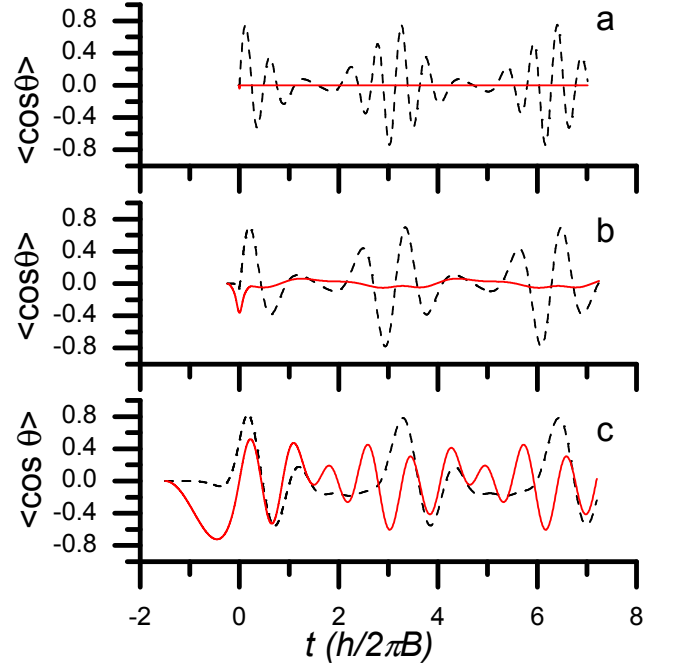


FIG. 2. (Color online). Orientation,  $\langle \cos \theta \rangle$ , for HCP pulses ( $\phi = \pi/2$  in Eq. (1)) for three different regimes showing the effect of the static component of the field. Solid lines correspond to calculations in which the dc component of the field has been removed, while dashed lines have been calculated including it. The parameters, in reduced units, for three pulses are: (a)  $\sigma = 0.006$ ,  $T = 0.04$ ,  $\omega = 200$ ,  $\mu E_0/B = 1000$ , (b)  $\sigma = 0.07$ ,  $T = 0.5$ ,  $\omega = 30$ ,  $\mu E_0/B = 100$ , and (c)  $\sigma = 0.45$ ,  $T = 3$ ,  $\omega = 3$ ,  $\mu E_0/B = 12$ .

pulse. This dynamical symmetry does not constraint either the instantaneous orientations or the time average orientation during the pulse, except for Floquet eigenstates, contrarily to what has been implicitly assumed in previous studies. From a classical point of view, for each classical trajectory with orientation  $\theta(t)$  there exists another one with orientation  $\pi - \theta(t)$ . Although the average orientation in the classical ergodic limit is zero [9], in the quantum case a nonzero average during the time span of one or several pulses can arise because nondiagonal matrix elements of the operator  $\cos \theta$ , in the Floquet basis, can be nonzero. Thus, conservation of time-reversal parity does not forbid a net time average orientation if the initial state is a combination of several non-degenerate Floquet eigenstates as we show below.

Taking as initial state a rotational eigenstate and expanding it in terms of Floquet eigenstates the time-evolved wave function can be written

$$\Psi(t) = \sum_n \exp[-i\epsilon_n(t + T/2)] b_n \chi_n(t), \quad (4)$$

where  $b_n = \langle \chi_n(t = -T/2) | J, M \rangle$ , which gives for the instantaneous orientation

$$\langle \Psi(t) | \cos \theta | \Psi(t) \rangle = \sum_{nm} \exp[i(\epsilon_n - \epsilon_m)(t + T/2)] b_n^* b_m O_{nm}(t), \quad (5)$$

with  $O_{nm}(t) = \langle \chi_n(t) | \cos \theta | \chi_m(t) \rangle$ .

Floquet eigenstates, in the extended Hilbert space, can be symmetric or antisymmetric with respect to time-reversal parity,  $\hat{\chi}(\theta, t) = \pm \hat{\chi}^*(\pi - \theta, -t)$ . Using this fact and the property  $E^*|J, M\rangle = (-1)^{J+M}|J, M\rangle$ , it can be shown that the coefficients  $d_{Jn}$  in Eq. (2) are imaginary for  $J$  odd and real for  $J$  even or viceversa depending both on the symmetric or antisymmetric character of the Floquet eigenstate and on the  $M$  value of the initial state. This implies for the coefficients of the eigenstates of  $U$  that  $c_J(t) = (-1)^{(J+k)} c_J^*(-t)$ , where  $c_J = \sum_n d_{Jn} \exp(2\pi i n t / T)$ . The integer  $k$  is zero for some eigenstates and one for others, resulting in  $O_{nn}(t) = -O_{nn}(-t)$ , and  $O_{nm}(t) = -(-1)^{(k_n+k_m)} O_{nm}^*(-t)$ . Taking into account  $O_{nm}(t) = O_{mn}^*(t)$ , the time average over the pulse duration of  $\langle \cos \theta \rangle(t)$  can be obtained integrating exclusively over the second half of the pulse

$$\langle \langle \cos \theta \rangle \rangle = \frac{1}{T} \int_0^{T/2} dt \sum_{m>n} A_{nm} \Theta[O_{nm}(t) \exp[i(\epsilon_n - \epsilon_m)t]], \quad (6)$$

where  $\Theta[\cdot] = \text{Re}[\cdot]$  if  $k_n \neq k_m$ , and  $\Theta[\cdot] = i \times \text{Im}[\cdot]$  if  $k_n = k_m$ , and the constants

$$A_{nm} = 2\{b_n^* b_m \exp[i(\epsilon_n - \epsilon_m)T/2]$$

$$- (-1)^{(k_n+k_m)} b_n b_m^* \exp[i(\epsilon_m - \epsilon_n)T/2]\}. \quad (7)$$

There is no symmetry relation between  $\langle \cos \theta \rangle(t)$  at any two different times greater than zero, and therefore the integral in Eq. (6) can be nonzero in spite of time-reversal parity due to the interference between pairs of Floquet eigenstates encoded in the  $O_{nm}$  terms. This mechanism can be loosely called transient breaking of time-reversal parity although, as we have shown, no symmetry is really violated. Fig. 3 shows the average orientation, during a rotational period, as a function of the field strength, for a sequence of ten pulses in panel a, and for a single pulse in panel b. For periodic sequences, equilibrium is reached after a few pulses since the average tends quickly to zero due to the growing phases in Eq. (6).

With current technology a strong single-cycle pulse can last no longer than a couple of ps, which seems to imply that obtention of a net average orientation over a time of the order of a rotational period would be possible by a single pulse only for the lightest molecules. However, the average orientation over a sequence of pulses is controlled by the differences between quasienergies unlike the average orientation over a single pulse, which is controlled by

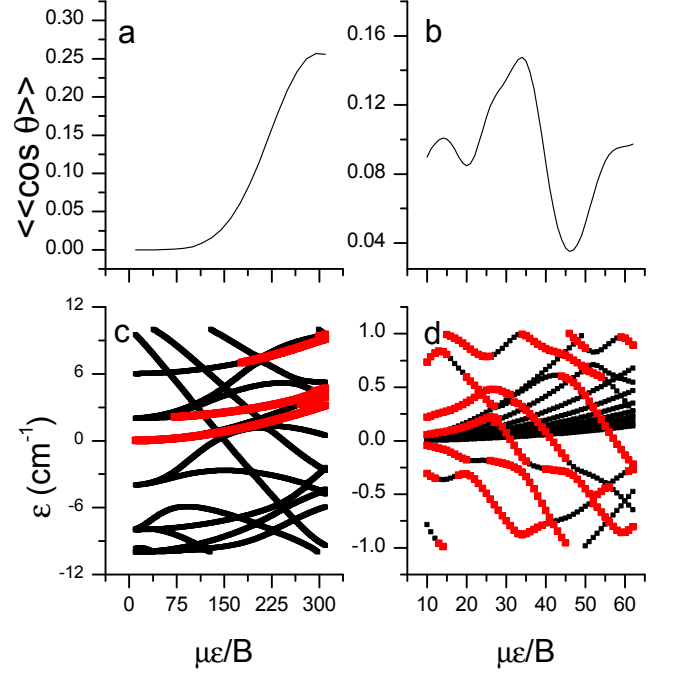


FIG. 3. (Color online). Time-average orientation,  $\langle \langle \cos \theta \rangle \rangle$ , over a rotational period, for two different regimes, as a function of field strength. Calculations were done by integration of Eq. (5) over the whole pulse. Parameters, in reduced units of time ( $\hbar/B$ ), are: (a)  $\sigma = 0.045$ ,  $T = 0.1\pi$ , and (b)  $\sigma = 0.45$ ,  $T = \pi$ . Thus, the time average in panel a corresponds to ten pulses and in panel b to one pulse. Panels c and d give the variation of the quasienergies with the field. Bigger (red) dots indicate the Floquet states with a greater contribution to the instantaneous wave packet.

the Floquet eigenvectors. Thus, a nonzero time average can be achieved by using sequences that span a rotational period as shown in panel a of Fig. 3. The only condition is being far from the sudden regime, otherwise the average orientation during each pulse will be very small. A greater stability in the average orientation is obtained with a sequence of pulses since the Floquet eigenvalues contributing to the instantaneous wave packets remain fairly constant with the field strength as shown in panel c of Fig. 3. On the other hand, for the longer pulse the existence of frequent avoided crossings (Fig. 3d) changes often the character of the Floquet eigenstates that form the wavepacket, giving rise to larger variations on average orientation. Ben Haj-Yedder et al. [25] explained that the most significant criterion for an efficiency-duration compromise regarding orientation phenomena, would be the maximization of the time average of  $\langle \cos \theta \rangle$  over a rotational period. In the absence of an external field, orientation-dependent properties, averaged over the rotational period, vanish. Such efficiency criteria cannot be used for orientation strategies based on HCPs because in that case orientation is achieved under effective field-free

conditions, i.e., during the weak long tail. However, the criterion is meaningful for single-cycle pulses.

Some confusion seems to exist in the bibliography concerning the symmetry properties that an external field must hold to orient a molecule. Two main consequences have resulted for the emerging field of THz quantum control: (i) explanation of the orientation mechanism with HCPs based on their intrinsic time asymmetry, (ii) disregard for single-cycle pulses of ps duration and zero CEP as an option for orienting molecules. This is due, as we have shown here, to the fact that HCPs much shorter than the rotational period give rise to molecular orientation because they contain a strong static component that produce a Stark effect. This component is not a solution of Maxwell's equations and cannot propagate with the pulse, so the mechanism is an unphysical artifact. In the far field limit the pulse will be distorted and the dc component is filtered out. The resulting propagated

pulse will then be unable to orient molecules. Contrarily, the regime where the pulse duration is comparable to the rotational period shows, for pulses of zero CEP, that the molecule gets sequentially oriented and antioriented as the dipole force breaks parity. Interference among Floquet states causes a transient breakdown of time-inversion parity leading to significant average orientations for times similar or longer than a rotational period; a phenomenon impossible to obtain in the sudden regime with half-cycle pulses. The average orientation for a long sequence of pulses remains zero as corresponds to the equilibrium or long-time limit, due to the fact the interference terms accumulate large phases when time progresses [9].

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